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FEASIBILITY OF LABORATORY AND ASTROPHYSICAL OBSERVATION

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ROTATIONAL AND VIBRATIONAL SPECTRA OF MOLECULAR IONS:

FEASIBILITY OF LABORATORY AND ASTROPHYSICAL OBSERVATION [*]

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ABSTRACT

The rotational spectra of a number of small molecular ions should be detectable in the microwave or millimeter wave regions in laboratory experiments using currently available techniques. The dipole moments and absorption coefficients of polar diatomics (e.g., CO^+ and NO^+) as well as asymmetric isotopically-enriched species, like $(^{18}O^{16}O)^+$, $(^{20}Ne^{22}Ne)^+$ and $(^{18}OC^{16}O)^+$, are calculated to be sufficiently large to allow observation of their spectra. In addition to the detailed molecular structure information which such spectral data would provide, precise knowledge of the transition frequencies would render likely the detection of certain of these ions in interstellar sources or in planetary atmospheres. All of these ions also possess vibrational spectra which should be detectable in the infrared region in laboratory or astrophysical sources.

INTRODUCTION

Rotational transitions of molecular ions have apparently not been observed either in the laboratory or in natural sources. Infrared transitions have been reported only recently [1] for the simplest of all molecular ions, HD^+. There is no fundamental reason why microwave or ir spectra should not be observable for a variety of ions, however; investigations toward this end are being pursued in several laboratories and observatories . This note considers some of the theoretical and experimental requirements of such observations. It will be shown that the microwave lines of ionic radiators in an environment of neutral perturbers are narrow enough to be observable. Microwave and ir transitions of <u>homonuclear</u> diatomic ions which have been isotopically asymmetrized should also be detectable. Consideration is given to several aspects of the laboratory, astrophysical, and aeronomical observation of ionic molecules.

MICROWAVE LINEWIDTHS

A crucial parameter determining the intensity of microwave absorption or emission in both laboratory and astrophysical sources is the linewidth parameter, $\Delta\nu$. In order for the spectroscopy of ions to be possible, their $\Delta\nu$ must be comparable to that for typical neutral molecules. The most important contributions to $\Delta\nu$ for neutrals arise from binary collisions which disturb the rotational state of the radiator and therefore broaden the line. There are two principal differences between ion-neutral and neutral-neutral collisions: (1) for an ion-neutral system the intermolecular forces are of longer range because of charge-multipole and

charge-induced multipole interactions, and (2) there is the possibility of charge exchanging collisions.

The contribution of long-range forces to $\Delta\nu$ may be estimated using the Anderson pressure-broadening theory [2]. One finds that for an ionic radiator and a neutral perturber, the charge-(induced) multipole forces do not contribute to the $\Delta\nu$ for the ionic transitions, at least through second order. Physically this is because such forces do not produce a torque on the ion. On the other hand the monopole of the ion does exert a torque on a neutral polar molecule, so that microwave lines originating from the neutral perturber are stark-broadened. However for the ionic lines and polar neutral perturbers, the dominant broadening mechanism is the dipole-dipole (R^{-4}) force [3]. For collisions of an ionic radiator with a non-polar perturber (such as H_2 in the interstellar medium) the dominant source of broadening is the dipole-quadrupole (R^{-5}) force [3]. The leading long-range broadening mechanism which does not occur in neutral-neutral collisions is the dipole-charge-induced dipole (R^{-6}) force [3].

As a specific example, the Anderson theory leads to an estimate of the dipole-dipole broadening for the $J = 0 \rightarrow 1$ transition in CO^+ ($\mu \cong 2.5$ D [4]) perturbed by CO ($\mu = .11$ D) of $\Delta\nu = 1.7$ MHz/Torr (at 300K). This is actually somewhat smaller than typical neutral linewidths (due to the small dipole moment of CO). However, inclusion of higher order dipole-quadrupole forces would increase the estimate of $\Delta\nu$ somewhat.

The other broadening mechanism to be considered is that of charge-exchanging collisions, which completely interrupt the radiation process. For thermal and low-

temperature systems, charge exchange cross sections for non-resonant collisions are negligibly small but resonant charge exchange cross sections are significant. They may be estimated on the basis of impact theory [5]. For the atom-atom case, at room temperature these cross sections are in the range $30\text{-}100\overset{\circ}{A}{}^2$, yielding $\Delta\nu$ values comparable in magnitude to the above-calculated Anderson-theory multipole broadening cross sections.

In summary, the linewidth for ions should be comparable or only slightly larger than for neutrals (due to charge exchanging collisions).

HOMONUCLEAR DIATOMIC IONS

The spectroscopy of some conventional diatomic ions is discussed below. However, a general class of ions which should be observable is that of homonuclear diatomics which have been asymmetrized by isotopic enrichment. The corresponding ion which contains two different isotopes possesses a dipole moment relative to the center of mass (because the center of mass and center of charge do not coincide [6]). Since the dipole moment varies periodically with the ion vibration, rotational and vibrational spectra are allowed. *

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*Recently there has been a report of ir emission spectra of HD^+ in a gas discharge laser [1], and of a device for analysis of HD by ionization and subsequent detection of HD^+ via ir absorption [7]. Note that the ir emissivity of neutral HD (which has a finite but very small dipole moment), has been calculated to be sufficient to justify astrophysical interest [8].

Estimates of the intensity of absorption or emission, relative to that for typical neutral polar molecules, are easily obtained. The dipole moment of a homonuclear diatomic ion of charge $Q = Ze$ containing isotopes of masses m_1 and m_2 separated by a distance R is given by

$$\mu(D) = 1.201 \, Z \, \frac{\Delta m}{\overline{m}} \times R(\overset{o}{A}) \tag{1}$$

where $\Delta m = m_1 - m_2$ and $\overline{m} = (m_1 + m_2)/2$. (Note that this expression is exact within the Born–Oppenheimer approximation, and is valid irrespective of the electronic state of the molecule.) The intensity of microwave absorption is proportional to the square of μ evaluated at the equilibrium bond length R_e, namely $\mu_e = \mu(R_e)$. The intensity of the fundamental ir transition is proportional to the square of the dipole derivative

$$\mu_e' \, (D \overset{o}{A}{}^{-1}) = 1.201 \, (Z\Delta m/\overline{m}) \quad . \tag{2}$$

Values of μ_e and μ_e' for first row diatomic ions (and for the linear symmetric triatomic CO_2^+) are given in Table I, along with typical values of these quantities for neutral polar molecules. Other factors being equal, the intensity of absorption or emission is somewhat less for the isotopically asymmetric ions than for hetero-diatomic ions or for typical polar molecules.

LABORATORY MEASUREMENTS

One straightford possibility for laboratory observation of rotational transitions of ions is the detection of absorption of microwaves passed directly through

the plasma of a glow discharge containing the ions [9,10]. (Other configurations

for production of the plasma or the absorbing ions are also possible.) As in experi-

ments with neutral species, the crucial quantity determining detectability is the peak

absorption coefficient, γ_{max}. For electric dipole transitions γ_{max} is given

by [11]:

$$\gamma_{max} = \frac{3\pi^2 Nf \,|\mu_{ij}|^2 \,\nu^2}{3ckT \,\Delta\nu} \tag{3}$$

where N is the number density of ions, f the fraction in the lower state of the

transition, μ_{ij} the dipole matrix element, $\Delta\nu$ the linewidth; remaining param-

eters have their usual meaning [11].

The most serious limitation relative to that of neutral species arises from

the smaller value of N, some four orders of magnitude less than the neutral density

(in the slightly-ionized plasmas suitable for microwave spectroscopy [9,10]). The

remaining factors in γ_{max} are comparable for ionic and neutral species. The

dipole matrix element $|\mu_{ij}|^2$ is proportional to the square of the dipole moment,

measured relative to the center of mass of the ion. Although experimental values

are not available, computed dipole moments of ions are similar to those of typical

neutral polar molecules [13].

A particularly favorable case* is CO^+, whose dipole moment has been

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*As an example, for the apparatus of Ref. 11, a 400 ma discharge through CO at

10 millitorr and room temperature should produce a fractional ionization of ca. 10^{-5}

with about half the ions being CO^+ [14]. Assuming $\Delta \nu \simeq 0.15$ MHz, Eq. 3

yields $\gamma_{max} = 10^{-7}$ cm^{-1} for the stronger member of the ρ-doublet of the

$0 \rightarrow 1$ transition of $CO^+ (X^2\Sigma^+)$ at 118 GHz.

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calculated [4] to be about 2.5 D (cf. the dipole moment of neutral CO, only

0.1 D), implying a relatively large value of $|\mu_{ij}|^2$. Other simple ions which

appear detectable are $NO^+ (X^1\Sigma)$ and $HF^+ (X^2\Pi)$ which should have a lambda-

doubling spectrum similar to OH.

The current practicality of laboratory measurements on the various

ions of Table I varies considerably from case to case for spectroscopic and

chemical reasons. Some of the ions (related to the solid elements) are

difficult to produce, but others, such as N_2^+, are the predominant ions in

discharges through gases not subject to chemical decomposition and thus

chemically more favorable than the heteropolar ions. The isotopic

homopolars would, consequently, appear to represent an important class of

ions for microwave experiments.

In addition to questions of intensity, spectroscopic considerations include

accessibility of the frequency range, accuracy of initial estimates of transition

frequencies (from optical or other data), and suitability of the transition for Zeeman

modulation.

Nitrogen and oxygen ions have similar rotational constants, but O_2^+ has a

$^2\Pi$ ground state, so that the first rotational transition is at 3B (143 GHz) (the

first transition with a Zeeman effect is at 5B), while in N_2^+ (a $^2\Sigma$ ground state)

there is a line at 2B (111 GHz) with a favorable Zeeman effect. This latter $0 \rightarrow 1$

transition of $(^{14}N^{15}N)^+$ is a particularly favorable case. Compared with the

previously discussed transition in CO^+ (isoelectronic with N_2^+) there is a decrease in intensity due to hyperfine splittings and the lesser dipole moment (with some compensating increase due to reduced $\Delta\nu$). This brings γ_{max} to ca. $10^{-10}\,cm^{-1}$, which is inadequate, but an increase in the fractional ionization and/or a decrease in the temperature (to $77^\circ K$) could increase this estimate by a factor of 10^2 or 10^3. Another favorable ion is $(^{20}Ne^{22}Ne)^+$, which should have no hyperfine splittings, a larger dipole moment, less line broadening, and higher K transitions at a given frequency. The isotopically asymmetric CO_2^+ ion is also a possibility, especially since a 50% concentration of the $^{16}OC^{18}O$ species should be readily obtainable [15], e.g., by isotopic exchange in the discharge:

ASTROPHYSICAL SOURCES

The possibility of observation of rotational transitions of ions present in the interstellar medium has attracted interest recently [16]. Such studies would naturally be facilitated by prior laboratory observation, obviating the requirement of searching in both frequency and in location. The microwave emission intensity from such sources depends on the product of the optical depth and the degree of excitation of the source molecules [16b]. The degree of excitation depends on a balance between collisional excitation (e.g., by hydrogen) and radiative relaxation (emission of microwave photons). Since strongly polar molecules have short radiative lifetimes, their state temperatures are lower and thus their signals weaker than for less polar molecules. Thus, the limitation of small dipole

moments * (e.g., for the enriched homonuclear ions) is not so disadvantageous.

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* Indeed, among the neutrals, $CO(\mu = 0.11 \text{ D})$ is a strong emitter with high state temperatures.

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The cross section and thus the probability of rotational excitation of an ion (e.g., CO^+) in a collision with a molecule, say, H_2, should be similar to that for a neutral, based on the discussion of $\Delta\nu$ given above and on available evidence from inelastic scattering experiments [17]. The parameter limiting observability, then, is the column density, with the requirement on it similar to that for neutral polar molecules.

One ion known to be present in interstellar clouds is CH^+, as detected optically long ago [18]. According to the theory of Solomon and Klemperer [19], this ion is the precursor of a chain of other molecules [20]. Unfortunately, CH^+ is a poor case for rotational spectroscopy because of its short radiative lifetime and low state temperature. A more favorable * possibility is C_2^+, predicted [19] to be at substantial abundance levels in HI regions.

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* Although laboratory studies of this ion are difficult due to chemical instability, the spectroscopic constants are known approximately from the optical spectrum of Meinel [21], if one assumes that the observed $^2\Pi_u$ lower state is in fact the ground state.

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A great many ionic species (including negative ions [22]) have been postulated as reaction intermediates in theoretical models of interstellar clouds, but little is known about their column densities. Klemperer [23] has postulated that the HCO^+ ion is responsible for the "X-ogen" line found in nine sources [24]. Dalgarno et al. [25] suggest that HCO^+ is widespread and abundant due to the fast chemiionization reaction of $O + CH$. There has been a recent calculation [26] of the radiofrequency spectrum of H_2D^+, believed to be an important constituent of interstellar clouds.

In view of the great diversity of the interstellar medium and of the chemistry of differentiation, it is probably that sources exist for several molecular ions with a steady-state ion density at the detectable level.

AERONOMICAL SOURCES

O_2^+ and N_2^+ are known to be abundant in the D and E layers of the earth's ionosphere [27,28] with O_2^+ second only to the polar NO^+ in the daytime. The negative ion O_2^- is also present in the D region [28]. The ionosphere of Jupiter is believed to be rich in H_2^+ (thus HD^+) [29] and the UV dayglow from the atmospheres of both Mars and Venus shows identifiably resolved CO_2^+ emission [29]. Undoubtedly C_2^+, C_2^- and HD^+ are plentiful in solar emissions. This suggests that satellite-based microwave and infrared studies of the atmospheres of the earth and other planets will lead to the detection of the spectra of a number of interesting molecular ions.

CONCLUDING REMARKS

Semiquantitative consideration has been given to the problem of the detectability of rotational and vibrational spectra of molecular ions in laboratory, astrophysical and aeronomical sources. When one includes the class of isotopically asymmetrized homonuclear ions one has a wide variety of possibilities warranting experimental investigation.

ACKNOWLEDGMENT

Table I. Values of Dipole and Dipole Derivatives of

Isotopically Asymmetric Ions.[a]

Ion	R_e [Å]	B_e [GHz]	ω_e [cm⁻¹]	μ_e [debye]	μ_e' [debye/Å]
HD⁺	1.06	675	2007.9	0.85	0.80
(^{3}He^{4}He)⁺ [b]	1.08	253	1755.2	0.37	0.34
(^{6}Li^{7}Li)⁺ [c]	3.08	16.5	---	0.57	0.18
(^{9}Be^{10}Be)⁺	--	--	--	0.13R_e[Å]	0.13
(^{10}B^{11}B)⁺	--	--	--	0.11R_e[Å]	0.11
(^{12}C^{13}C)⁺ [d]	1.30	48.0	1320	0.14	0.10
(^{12}C^{13}C)⁻	1.27	50.4	1746.4	-0.14	-0.10
(^{14}N^{15}N)⁺	1.12	55.6	2170.2	0.09	0.08
(^{16}O^{17}O)⁺	1.12	48.9	1876.8	0.08	0.07
(^{16}O^{18}O)⁺	1.12	47.6	1851.3	0.16	0.14
(^{16}O^{17}O)⁻	1.31	35.8	1091	-0.08	-0.07
(^{16}O^{18}O)⁻	1.31	34.8	1176	-0.16	-0.14
(^{20}Ne^{22}Ne)⁺ [e]	1.7	17.0	645	0.19	0.11
(^{16}O^{12}C^{18}O)⁺ [f]	1.78	10.8	1244	0.25	0.21
Typical heteronuclear neutral diatomic [g]				0.1-3.0	0.2-6.0

[a] Data obtained from reference 30 except where noted. (Corrected for isotopic substitution.)

[b] Reference 31.

[c] Model calculation, reference 32.

[d] Tentative assignment, reference 21.

[e] Reference 33.

[f] Reference 34.

[g] Reference 35.

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